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(57) Abstract

Wet edible collagen casings of high moisture content (e.g. 50 to 90 % by weight) have mechanical properties which allow the casing to be filled with meat or other filling in the wet state. The wet casings are not subjected to a conventional hot air drying step. The casings are produced by extruding an acidic collagen gel, followed by coagulation using ammonia. A cross-linking agent such as glutaraldehyde may be included in the extruded gel or may be used as in a bath to treat the coagulated casing. The cross-linked casing is then treated to remove some of its water content and to reduce its thickness using a brine bath, a chemical dehydrating agent such as carboxymethyl cellulose; or a combination of these treatments. Improved elasticity is imparted by subjecting the casing to a heat treatment step under conditions of time and temperature which lead to heat shrinkage of the casing. The wet casing has handling and filling properties which approximate those of natural gut casings.

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SUMMARY OF THE INVENTION

The present invention provides a wet edible collagen casing which has been continuously formed and cross-linked, such that the casing has mechanical properties allowing the casing to be filled in its wet state, the casing being packed in its wet state ready for use.

By "wet" condition we mean that the casing has a high water content compared with conventional dried collagen casings used for sausages. Typical mechanically dried conventional casings have a water content in the region 15 to 25%. The wet collagen casing of the present invention may have a water content of 50 to 90%, preferably 70 to 90% by weight.

The collagen casing packed in its wet condition may be stored in brine and suitable additional bacteriocides may be added if required.

However, in a preferred embodiment the collagen casing is packed in its wet state (i.e. at a high moisture content) but is not surrounded by liquid. For example, the wet casing may be packed within a hermetically sealed pouch formed of a conventional material such as a plastics coated foil.

The wet casing of the present invention has mechanical properties which enable it to be filled and used in a manner analogous to natural gut. However, the

present wet casing has the advantage of greater uniformity of bore, can be produced in any desired length and is generally capable of being filled at faster speeds than natural gut casings. Using the present invention speeds of at least 150 links per minute may be achieved using a Handtmann FA30 or PA30 sausage filling machine.

Generally the wet casing has a solids content of 15 to 30%, preferably 20 to 25% by weight, the balance being water; in comparison to a value of about 10 to 30% by weight for washed unsalted natural gut (but typically 15-25% by weight). The collagen content of the wet casing is usually 9 to 14% by weight; which is comparable to natural gut. Cellulose may be included; but where high collagen contents are required, the cellulose content may be reduced or omitted.

Usually the balance of the solids content is comprised of salt e.g. sodium chloride, in an amount of 5 to 15% of the total weight.

The present invention also provides a process for the production of a wet edible collagen casing which comprises:

- forming an aqueous collagen gel into a continuous casing;
- cross-linking the casing by use of a cross-linking agent;
- treating the casing with a salt solution to remove water and to reduce the wall thickness of the casing; and
- packing the casing in the wet state.

Preferably, the collagen gel is an acidic gel having a pH in the range 2 to 5. It may also include conventional additives such as polyols (e.g. glycerol and sorbitol), modified celluloses, charged polysaccharides (e.g. sodium carboxyalkylcelluloses) or uncharged polysaccharides (e.g. hydroxypropyl methyl cellulose).

The acid collagen gel may be produced using known techniques such as by subjecting limed hide splits to washing, decalcification, mincing, grinding with water and acidifying to produce a fibrillar gel; or by washing, decalcifying, acidifying and grinding (e.g. using Fryma grinder) followed by kneading with a controlled amount of water to form a more fibrous gel (e.g. for use in larger diameter casings).

Usually, the gel contains 3 to 12 wt% collagen, preferably 4.5 to 10 wt%.

The casing may be continuously formed by extrusion, spinning or other known means.

The casing may be hardened in conventional manner by passing a mixture of air and ammonia into the lumen of the casing and maintaining an ammonia atmosphere around the outside.

The cross-linking agent may be any acceptable cross-linking agent known in the art but is preferably a dialdehyde such as glutaraldehyde or glyoxal, or a multivalent metal ion such as aluminium. In a preferred embodiment, the cross-linking agent is present in an aqueous solution through which the casing is passed; and

is for example an aqueous solution of 10 to 3000 ppm glutaraldehyde, preferably 25 to 200 ppm, and the residence time of the casing is from 2 to 10 minutes, preferably 4 to 8 minutes. The aqueous glutaraldehyde bath is usually at a pH 5 to 10, preferably 8 to 10. Alternatively, the cross-linking agent may be included in the gel prior to extrusion; for example in an amount of 0.1 to 0.6 wt % in the case of glutaraldehyde.

After cross-linking, the casing may be partially chemically dried employing a carboxymethyl cellulose or sodium alginate solution. The solution preferably comprises 0.5 to 2.5% weight of the chemical dying agent and is preferably used at a temperature of 15° to 50°C.

The casing is treated with a salt solution to reduce the wall thickness of the casing, such that the thickness approaches that of natural casings of the same overall diameter. Typically, the wall thickness is reduced from 0.3-0.6 mm down to 0.1 to 0.2 mm. The salt may be any suitable salt known in the art but is preferably sodium chloride. Advantageously, the salt solution comprises 10 to 25% by weight of salt. Salt treatment may be carried out at 15 to 35°C, elevated temperatures aiding dehydration.

The salt solution also has the effect of improving the feel of the casing and thereby improving its handleability. It may also improve the clarity of the casing.

The casing may be subjected to a heat shrink treatment for a time (e.g. 2 to 30 seconds) and at a temperature (e.g. 70 to 95°C, preferably 80 to 90°C) which reduces its volume and may remove water from the casing. This may be manifested as a reduction in length of the casing or its width (in the flat state), or even its thickness. The treatment is carried out at a temperature above the so called "heat shrink" temperature of the collagen. Shrinkage of collagen at elevated temperature is a well known phenomenum (see for example, "Chemistry and Technology of Leather", F. O'Flaherty, W.T. Roddy and R.M. Lollar, published by Robert Krieger, Chapter 16).

This temperature will depend on the degree of cross-linking of the collagen but can be determined by routine experimentation. Generally, lower temperatures will require long times, and vice versa, in order to provide an effective heat shrink treatment.

The heat shrink treatment is generally carried out in a water bath, and tends to increase the elasticity of the casing thereby more closely approximating natural casings, and also to improve its tensile strength. The heat treated casing thus behaves more similarly to natural gut casing.

The strength of the casing may be measured by the so-called "burst height" (as defined herein). Preferably the casings of the present invention have a burst height of at least 120cm, preferably at least 150cm. Increased burst heights are desirable since the casings have a

reduced tendency to burst on filling.

The elasticity of the casing may be estimated by the "blow value" (as defined herein). Preferred blow values are at least 30cm, preferably at least 40cm, and especially at least 50cm. Increased elasticity tends to more closely approximate the handling and filling properties of natural gut casings.

The wall thickness and mechanical properties of the casing of the invention will tend to be chosen to correlate with those of the equivalent natural product. For example, the properties may be chosen to correlate those of small diameter natural gut from a particular animal, or larger diameter gut from a larger animal. The finished wall thickness will usually be in the region 0.05 to 0.3mm depending on the diameter of the casing.

The casing is then packed in its wet state usually by either shirring, spooling or reeling the casing. Shirring means that the casing is accummulated in a rouched manner on a cylindrical former in a discrete length, typically 15 to 50 metres, and then removed from the former. The term spooling means that the casing is shirred onto a length of pipe, typically a plastic pipe, which is adapted to fit over a stuffing horn so that the length of casing may then be filled in a single continuous manner. The casing might also be reeled, that is to say, wound up in its flat state.

While reference has been made to sausages, the collagen casing of the present invention may be filled with other foodstuffs, such as hamburger meat, cheese

based fillings or vegetarian fillings.

The present invention avoids any costly mechanical drying step. Mechanical drying refers particularly to air drying or infra-red drying or equivalent means which are currently used in the production of existing dried collagen casings. In the present invention mechanical drying is avoided and thus the production energy costs are lower for the wet casing of the present invention than for standard dried collagen casings. Thus, using the present invention it is possible to produce wet casings which are similar to natural casings but at a cost which is comparable to that of natural hog gut. Using the present invention, the customer who normally prefers natural gut casing may be provided with a collagen product which has the advantages of uniform thickness and better diameter control whilst having substantially the appearance and feel of natural gut casings.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will now be described by way of example only in conjunction with the following example and drawing wherein:-

Figure 1 shows the variation in tensile strength of a cross-linked casing during production as described in Example 1; and

Figure 2 is a block flowchart of the process described in Example 4.

Example 1

Limed hide splits (i.e. the lower corium of the hide) were washed, decalcified with ammonium sulphate and citric acid, minced, ground and mixed with hydrochloric acid to produce a fibrillar collagen gel of pH 2.0 comprising approximately 6% collagen, 0.4% hydrochloric acid and 93.6% by weight water. The gel is aged by standing for one or two days, homogenised and then filtered. The gel is then passed through an extruder so that a tube is extruded. A mixture of air and ammonia gas is blown into the lumen of the tube at the extruder end, whilst the exterior of the tube is passed through an atmosphere which is primarily ammonia. At the end of the ammonia chamber the tube is flattened by nip rollers and passed through a water bath which washes the casing. The residence time in the water bath is 20 minutes and the solids content of the casing 6 to 8% by weight. The typical tensile strength is approximately 1.5 kg.

The casing is then passed through a bath containing 100 to 200 ppm glutaraldehyde for approximately 8 minutes in order to cross-link the collagen.

Next the casing is passed through a chemical drying bath comprising 2% weight sodium-carboxymethyl cellulose (CMC) at 35^{o}C for 20 minutes to remove water from the casing. The solids content is from 12 to 14% weight collagen. The tensile strength is approximately 2 to 2.5 kg.

The casing is then treated by passage through a bath comprising 20% aqueous sodium chloride at ambient temperature for 30 minutes which removes further water from the casing. The solids content of the casing is 11 to 14% weight collagen together with 10 to 14% weight sodium chloride. The tensile strength is approximately 2.5 to 3.5 kg. The wall thickness is approximately 0.14 mm.

Then the wet casing is removed from the bath and spooled in the wet condition on a plastic cylinder holding approximately thirty meters of wet casing. The wet casing is then packed in a sealed pouch and is ready for sale.

Table 1 shows typical compositions of wet casings according to the invention compared to natural hog and sheep gut casings (washed and unwashed).

TABLE 1.

	%NaCl	%Collagen	%Solids
Invention 1	12.72	10.74	23.32
Invention 2	12.87	9.91	21.99
Comparison			
(A) washed hog gut	17.46	12.03	32.53
(B) washed sheep gut	8.24	12.47	25.64

Table 2 shows the variation of solids content during the production process of the invention.

Table 2 (Solids Profile)

		Collagen wt%	NaCl wt%
(i)	pretreatment	7.7	0.01
(ii)	glutaraldehyde-treated	7.5	0.01
(iii)	CMC - treated	10.4	0.01
(iv)	NaCl-treated final product	10.9	12.7

Table 3 shows various physical properties of the wet casing (compared to hog gut) for 28mm diameter casings.

Table 3 (Physical Testing)

	Wet casing (invention)	Hog Gut
Tensile strength (cold) kg/cm^2	3.0 - 3.2	1.63
" " (hot acid) kg/cm^2	3.0	1.36
Weight g/m	16	8
Thickness microns	75 - 100	25 - 35

Both casings were capable of being filled at full speed on Handtmann FA30 or PA30 filling machines.

EXAMPLE 2

Limed hide splits, or other suitable collagen sources were washed, delimed with CO_2/ammonium sulphate and citric acid/Na citrate, minced, ground and mixed with hydrochloric acid to produce a fibrillar collagen gel of pH 2.0 comprising approximately 5% collagen, 0.25% hydrochloric acid and 94.75% by weight water. The gel is aged by standing for one or two days, homogenised and then filtered. The gel is then passed through an extruder so that a tube is extruded. A mixture of air and ammonia gas is blown into the lumen of the tube at the extruder end, whilst the exterior of the tube is passed through an atmosphere which is primarily ammonia. At the end of the ammonia chamber the tube is flattened by nip rollers and passed through a water bath which washes the casing. The residence time in the water bath is 20 minutes and the solids content of the casing 6 to 8% by weight. The typical tensile strength is approximately 1.8kg.

The casing is then passed through a bath containing 50 to 100 ppm glutaraldehyde for approximately 8 minutes in order to cross-link the collagen.

Next the casing is passed through a chemical drying bath comprising 2% weight sodium carboxymethyl cellulose (CMC) at 35^{o} for 20 minutes to remove water from the casing. The solids content is from 12 to 14% weight collagen. The tensile strength is approximately 2.5 to 3.5kg.

The casing is then treated by passage through a bath comprising 20% aqueous sodium chloride at ambient temperature for 30 minutes to remove further water from the casing. The solids content of the casing is 12 to 14% weight collagen together with 12 to 14% weight sodium chloride. The tensile strength is approximately 3.5 to 4.0 kg. The wall thickness is approximately 0.2 mm.

Then the wet casing is removed from the bath and spooled in the wet condition on a plastic cylinder holding approximately thirty meters of wet casing. The wet casing is packed in a sealed pouch and is ready for sale.

Table 4 shows various physical properties of the wet casing (compared to hog gut) for 35mm diameter casings.

Table 4 (Physical Testing)

	Wet Casing (invention)	Hog Gut
Tensile strength (cold) kg/cm^2	7.0 - 8.0 kg	1.5 - 2.3 kg
" " (hot acid) kg/cm^2	6.0 - 7.0 kg	1.3 - 1.6 kg
Weight g/m	40	10
Thickness microns	125 - 150	30 - 35

Both casings were capable of being filled at full speed on Handtmann FA30 or PA30 filling machines.

EXAMPLE 3 (liquid coagulation)

Limed splits were washed, cut into portions, approximately 25cm square, decalcified with hydrochloric acid and washed to remove salts for approximately 24 hours. The splits are comminuted and then acid swollen with hydrochloric acid to produce a gel of approximately 8-10% collagen, 0.8% HCl and 90% water. The gel is aged by standing for one or two days, kneaded, homogenised and filtered. The gel is then passed through an anular extruder into a saturated solution (40%) of ammonium sulphate at a pH of 9-9.5 so as to coagulate the gel. Ammonium sulphate solution is introduced to the lumen of the tube at the extruder and the diameter of tube is controlled by balancing internal and external flows. After coagulation the casing is flattened and then passed through a solution of 13% ammonium sulphate at pH of 8.5; and then through water baths for approximately 30 mins to wash the casing. The casing is then crosslinked by a solution of glutaraldehyde for approximately 10 minutes and transferred to a bath containing saturated brine solution to remove water from the casing. The solids content by weight of the casing is approximately 13-16% collagen with 10-15% of sodium chloride. The tensile strength is 7.0kg and wall thickness is 0.25 mm. The wet casing is then spooled on a plastic cylinder designed for the length required. The spool is packed in a sealed pouch ready for use.

EXAMPLE 4 (including heat treatment)

A flattened collagen casing, which had been treated with ammonia and washed in water, was produced in the general manner described in Example 1.

Collagen pulp and a water/acid mixture are blended together to form a gel of 5.80% collagen and 0.40% HCl. The gel then undergoes a double homogenisation at 4500 pounds per square inch with cooling.

However, in this case cross-linking with glutaraldehyde was carried out by injecting glutaraldehyde in an amount of 0.35wt % into the gel just prior to extrusion. The degree of cross-linking produced was comparable to that produced by using a glutaraldehyde bath in Example 1.

The cross-linked casing is then passed through a hot water bath at a temperature of about 80°C for 8-11 secs. in order to bring about a heat shrinkage of the collagen casing. This results in a shrinkage in the length dimension of the casing which results in a reduction of 20-40% in length. The width of the flattened tube was reduced by about 30%, but this was an elastic reduction - the original width being largely restored when the casing was finally filled with meat. The wall thickness of the casing was substantially unaffected.

Then the heat-shrunk casing is treated by passage through a brine bath comprising 20% aqueous sodium chloride at ambient temperature for 30 minutes.

The wet casing then removed from the brine bath and spooled or reeled; and is then packed in a sealed pouch ready for sale.

Figure 2 is a flowchart showing the various steps of the process. The filter bank for filtering the gel comprises first and second wirewound filters of mesh size 0.006 and 0.004 inch (152 and 101 microns). Glutaraldehyde cross-linking agent is injected into the gel just upstream of a gel metering pump (not shown). Heat shrinkage is carried out by passing the casing through a heated water bath in the region 80-95°C.

Tables 5 and 6 show the properties of various heat shrunk casings produc : by variations of the heat shrink bath conditions.

Within each series of tests at specified casing widths, experimental conditions (such as the extruder operating parameters, weight of gel extruded per unit length etc.) are maintained constant so that a direct comparison is possible. However, conditions may vary between series of tests so that comparisons between different series may not be meaningful. Nevertheless, it is clear that the heat shrink treatment tends to shrink the length and width of the casing, to increase its energy to breaking; and to increase its tensile strength, burst height and blow value. A decrease in modulus and thus increase in elasticity is also observed.

In edibility tests, a panel found little perceived difference between the tenderness of the wet casings of

the present invention and natural hog gut when the casings were filled with meat and cooked. The wet casings of the invention were able to be filled successfully.

Table 7 shows the improvement in mechanical properties as a function of increasing glutaraldehyde content in the extruded gel. The casing was heat shrunk for 12 sec. at 85°C. A general increase in all parameters is to be noted. However, levels of glutaraldehyde are preferably kept low to avoid undesirable residual unreacted glutaraldehyde in the finished casing.

Test Methods

(a) The tensile strength and elongation (i.e. strain) was measured using an Instron 1122 testing machine following the manufacturers recommendations. Instron is a trademark. The collagen film is cut in either the machine direction (MD) or transverse direction (TD) using a dumbbell-shaped cutter. Each dumbbell-shaped sample of film is tested using the precalibrated Instron tester. The sample is clamped into the machine and sprayed with water. The Instron tester pulls the sample until it breaks and the data is stored in the computer memory of the tester. The testing procedure may be repeated on a number of samples to give a statistically significant result. The computer program calculates modulus, energy to break, percent strain and maximum load.

(b) The burst height is the height (cm) of a water column (and therefore the weight of water) that the collagen casing will support when closed at the bottom end before the casing bursts. The burst height is thus a measure of the strength of the casing in both the machine and transverse directions. It indicates the ability of the casing to be filled at high fill pressures. A metal tube of approximately the same diameter as the casing is inserted into the open end of a length of casing 2.5 to 3 metres long, and it is suspended from that end in a test rig. The lower end of the casing is knotted about 2.5m below the top of the casing. Water at a rate of 1.5l/min is fed into the upper end of the casing until the casing bursts. The highest point of the water in the casing prior to burst is recorded. The burst height is the height of the water from knot to highest point.

(c) The blow value is a measure of how much the casing expands when filled out with a given volume of water to simulate filling with meat etc. A high value suggests a low elasticity and a high modulus, giving rise to a more rigid filling performance. A low value can lead to problems of over expansion of the casing when filled. A metal tube of approximately the same diameter as the casing is inserted into the

open end of a length (1 to 2m) of collagen casing, and suspended from that end in test rig. The lower end of the casing is knotted and a clip attached to hold the knot. A predetermined volume of water dependent on the diameter of the casing (200ml for 28mm, 300ml for 36mm, and 400ml for 40mm) at 25°C is quickly poured into the upper end of the casing. A timer is started as soon as the last of the water has been poured in. After exactly one minute the height of the column is marked. The distance (cm) between the knot and the marked height is the blow value.

(d) The hot acid tensile strength test is designed to measure the degree of cross-linking developed in the final casing. A 5 inch (128mm) long sample of casing is immersed in about 500ml of 0.1N HCl solution at 70°C±1°C for 60 seconds. The sample is removed from the solution and clamped in clamps exactly 2 inches (51mm) apart in an Instron tensile tester. The clamps are drawn apart in the tester at 500 mm/min until the sample breaks. The breaking strength is recorded. The test is repeated three times on the same sample and the average taken. The higher the breaking strength, the greater the degree of cross-linking of the collagen which has taken place.

TABLE 5 (heat treatment bath)

Initial width* mm	Time sec	Temp °C	%shrink (length)	Modulus** kg/mm^2	max load kg	%strain	Energy to break kg.mm	final width* mm	Blow value cm
44.5	5	70	-1	35.7	5.50	26.5	53.8	44.7	40.0
	5	80	-6	35.7	5.57	25.0	52.1	42.3	42.7
	10	70	-4	33.4	5.62	29.6	53.7	42.7	42.3
	10	80	-8	32.0	5.74	33.7	67.2	43.0	42.3
49.0	5	70	-4	33.4	5.08	26.6	52.6	47.0	33.0
	5	80	-9	32.8	5.20	30.1	55.2	46.3	33.3
	10	70	-2	31.1	5.20	30.9	56.9	47.3	33.7
	10	80	-36	20.0	6.08	55.4	104.9	42.0	44.3

* width of the flattened tube

** the elasticity is inversed proportional to the modulus.

TABLE 6 (effect of heat treatment)

Initial Width* mm	Time sec.	Temp °C	Cold Tensile kg/cm^2	Hot Acid Tensile kg/cm^2	Burst Height cm	Final Width* mm	Blow Value cm
49.0	none	none	4.66	4.00	133.7	52.7	29.4
49.0	12	85	4.88	4.31	202.3	34.7	61.3

TABLE 7 (varying glutaraldehyde)

Glutaraldehyde %wt of gel	Cold Tensile kg/cm^2	Hot Acid Tensile kg/cm^2	Burst Height cm	Width mm	Blow Value cm
Control	1.16±0.18	0.22±0.04	50.7±20	33.7	66.0±0.4
0.175%	3.73±0.68	2.70±0.52	112±3	36.5	75.8±0.7
0.350%	4.86±0.27	3.66±0.47	120±9	36.0	85.6±1.1
0.540%	4.20±0.74	3.84±0.43	130±2	40.4	74.8±1.3

CLAIMS

1. A wet edible collagen casing which has been continuously formed and cross-linked, such that the casing has mechanical properties allowing the casing to be filled in its wet state, the casing being packed in its wet state ready for use.

2. A wet casing according to claim 1 which has a solids content of 10 to 30% by weight, the balance being water.

3. A wet casing according to any preceding claim which has a collagen content of 9 to 14% by weight.

4. A wet casing according to claim 3 wherein the balance of the solids content consists substantially of edible salt.

5. A wet casing according to claim 4 wherein the balance of the solids content comprises 10 to 15% by weight sodium chloride.

6. A wet casing according to any preceding claim wherein the casing has a wall thickness of 0.1 to 0.2 mm.

7. A wet casing according to any preceding claim which is capable of being filled at a rate of at least 150 sausage links per minute.

8. A wet casing according to any preceding claim which has a burst height (as defined herein) of at least 120cm.

9. A wet casing according to any preceding claim which has a blow value (as defined herein) of at least 40cm.

10. A wet casing according to any preceding claim which has been heat shrunk.

11. A process for the production of a wet edible collagen casing which comprises:

- forming an aqueous collagen gel into a continuous casing;
- cross-linking the casing by use of a cross-linking agent;
- treating the casing with a salt solution to remove water and to reduce the wall thickness of the casing; and
- packing the casing in the wet state.

12. A process according to claim 11 wherein the salt solution is a sodium chloride solution.

13. A process according to any of claims 11 to 12 wherein the casing is cross-linked prior to treating with salt solution.

14. A process according to any of claims 11 to 13 wherein the cross-linking agent is glutaraldehyde.

15. A process according to any of claims 11 to 14 wherein the aqueous collagen gel comprises 3 to 12% by weight collagen.

16. A process according to claim 15 wherein the gel comprises 4.5 to 10% by weight collagen.

17. A process according to any of claims 11 to 16 wherein the cross-linked casing is subjected to chemical drying to reduce its water content.

18. A process according to claim 17 wherein the chemical drying agent is sodium-carboxymethyl cellulose.

19. A process according to any preceding claim wherein the cross-linked casing is heat treated in water to reduce its volume.

20. A process according to claim 19 wherein the heat treatment is above the heat shrink temperature of the cross-linked collagen casing.

21. A process according to claim 19 or 20 wherein the heat treatment is for 2 to 30 seconds at a temperature of 70 to 95^{o}C.

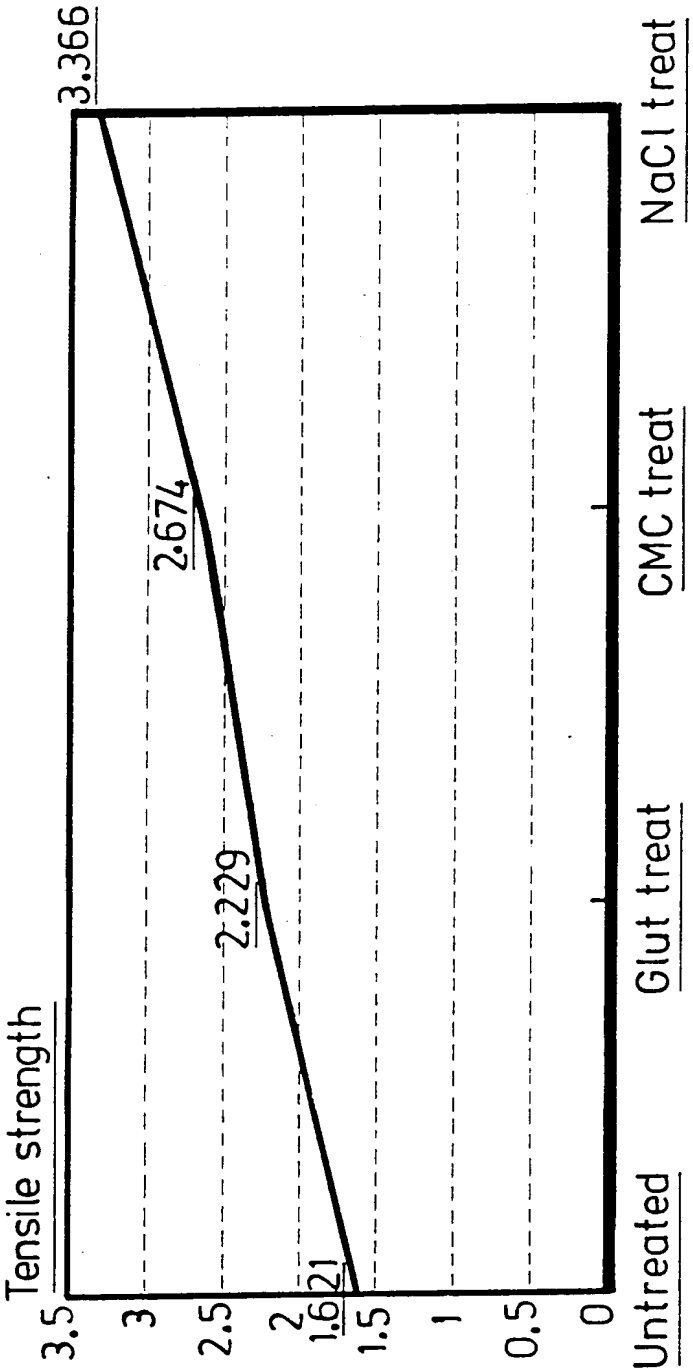
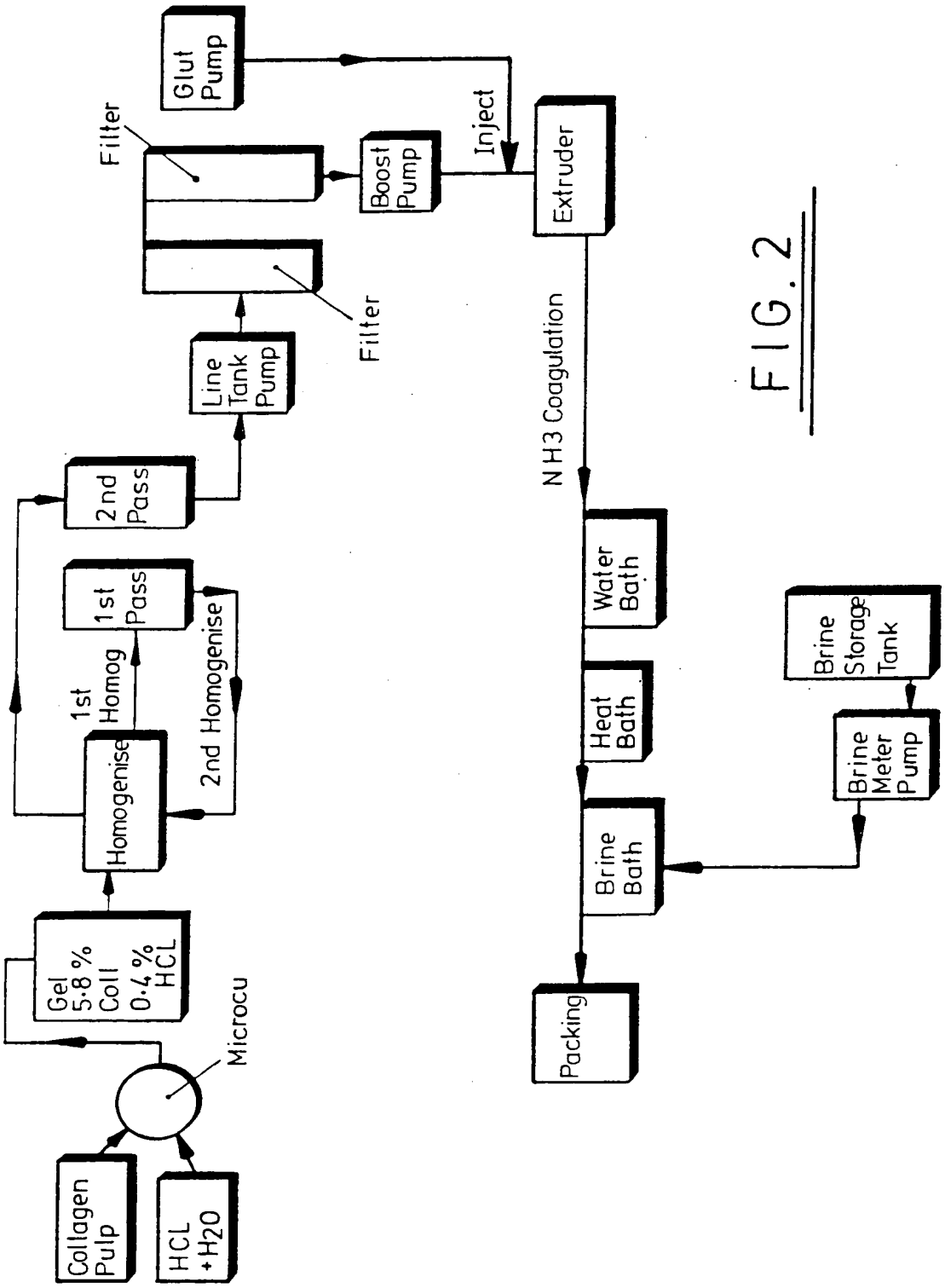

Tensile strength
3.5
3
2.5
2
1.621
1.5
1
0.5
0
3.366
2.674
2.229
Untreated
Glut treat
CMC treat
NaCl treat
Treatment

FIG. 1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Gel 5.8 % Coll 0.4 % HCL
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Filter
Filter
Glut Pump
Boost Pump
Inject
Extruder
NH3 Coagulation
Water Bath
Heat Bath
Brine Bath
Packing
Brine Storage Tank
Brine Meter Pump

FIG. 2

INTERNATIONAL SEARCH REPORT

national Application No
PCT/GB 93/02045

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A22C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 A22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8001, 19 November 1979 Derwent Publications Ltd., London, GB; Class D12, AN 80-00772C NITTA GELATIN KK & JP,A,54 147 968 (NITTA GELATIN KK) see abstract ---	1-21
A	US,A,3 235 641 (MC KNIGHT) 15 February 1966 cited in the application see claims; examples ---	1-21
A	US,A,3 930 035 (BURKE ET AL.) 30 December 1975 cited in the application see claims --- -/--	1-21

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 February 1994	14. 03. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Kaumann, E

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 93/02045

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 083 126 (VAESSEN-SCHOEMAKER HOLDING B.V.) 6 July 1983 see the whole document ---	1,11-13
A	FR,A,2 172 273 (NATURIN-WERK BECKER & CO.) 28 September 1973 see claims -----	1,11-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

.rnational Application No
PCT/GB 93/02045

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